On the Motion of Fullerenes Around Topological Defects on Metals: Implications for the Progress of Molecular Scale Devices.

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Abstract

Research on motion of molecules in the presence of thermal noise is central for progress in two-terminal molecular scale electronic devices. However, it is still unclear what influence imperfections in bottom metal electrode surface can have on molecular motion. Here, we report a two-layer crowding study, detailing the early-stages of surface motion of fullerene molecules on Au(111) with nanoscale pores in a *n*-tetradecane chemical environment. The motion of the fullerenes is directed by crowding of the underlying *n*-tetradecane molecules around the pore fringes at the liquid-solid interface. We observe in real-space the growth of molecular populations around different pore geometries. Supported by atomic-scale modelling, our findings extend the established picture of molecular crowding by revealing that trapped solvent molecules serve as prime nucleation sites at nanopore fringes.

A classical crowded system is one in which the spacing between adjacent agents is equivalent to the individual agent dimension (*van-der-Waals* diameter in the case of molecular systems, Fig.1a) thereby maximising the volume (entropy) available to them which minimises steric excluded volume effects (free energy). The fundamental difference between a crowded[1-4] and a self-assembled molecular system[5-7] is the absence of orientational order in a molecular crowd. By contrast, molecules can self-assemble into highly-ordered configurations after stochastically exploring parallel configurations *en route* to thermodynamic minimum[8]. Yet, to clearly delineate the interfacial physics governing crowding of nanometre sized molecules on surfaces there is a pressing need for metrology tools capable of resolving molecular processes in real-world environments. One such model research tool is a combined scanning tunnelling microscope (STM) and spectroscope (STS) that can electronically and structurally fingerprint molecules[9-12] with nanoscale spatial sensitivity in liquids at room-temperature. There have been major advances in liquid-STM/STS based studies to probe both sparse (Fig. 1b) and crowded (Fig. 1c) molecular systems on defect free metal thin films[7, 12-15] and gauge the impact of solvent on self-assembled end structures[11, 16-17]. Nevertheless, the early-stage dynamics of molecules is still poorly understood, particularly non-linear interactions of single-molecules interfacing with surface defects on metals. In this work we explore a means of using a self-assembled molecular system of solvent on Au(111) with nanopore topological defects as a platform to create a crowded system of fullerene (C_{60}) molecules through pinning of a thin layer of solvent molecules to the fringes of the nanopores. To this end, we have conducted liquid-based structural and spectroscopic analysis of single-molecular binding and molecular ensemble crowding events at nanoscale pores on Au(111) in a liquid environment. The nanopores formed by the Zener pinning mechanism[18-19] during metal thin film growth on mica and display a range of geometries with different pore diameters and depths. We then

rely on molecular dynamics simulations to reveal the atomic-scale details of the molecular dynamics around pore fringes at experimentally inaccessible nanosecond timescales.

Figure 1d is a schematic depiction of our STM/STS experimental setup. A mechanically cut Pt/Ir wire is employed as the STM probe. The Au(111) surface with nanoscale pores serves as the surface platform positioned inside a Teflon-based liquid-cell holder. A 10^{-2} M concentration C_{60} solution is injected on the surface and fills the probe-sample tunnel gap at the apex of the STM probe. The electron tunneling mechanism (schematic in Fig.1e) through *n*-tetradecane[20] is comparable to quantum mechanical tunneling through a vacuum barrier as the liquid molecules do not interfere electronically with the tunneling current which tends to decay exponentially as a function of probe-sample distance even within a non-polar liquid environment. Figure 2a is a wide-angle constant current STM image showing regions of C_{60} molecules immediately after injection of the solution comparable to previous STM studies of C_{60} dynamics at the liquid-solid interface[8]. From this STM image a lack of directional ordering of molecules is evident, as is a lack of any evidence for close packed structures. Spatially magnifying within the initially imaged large area shows the pinning of either a few C_{60} molecules or a single C_{60} molecule at the pore fringes (Fig. 2b and Fig. 2c). These high-resolution STM images of C_{60} molecules pinned at nanopore fringes (nanopore defect density is 80 ± 10 per 500 nm^2) also reveal a disordered array of surrounding molecular elements. Similar images were recorded at other nanopore locations, which suggests two possibilities for the origin of the observed disordered molecules, the first being an underlying layer of disordered C_{60} molecules. However, the observed level of disorder could also stem from imaging a second layer of disordered solvent molecules as the first layer of *n*-tetradecane on Au(111) tends to form an ordered monolayer at room-temperature[12, 21,10, 20, 22-23.]

In an effort to resolve this question, we combine structural analysis with spectroscopic electronic fingerprinting to differentiate the guest (C_{60}) and host (*n*-tetradecane) molecules. After positioning the STM probe on top of a single C_{60} molecule (indicated by the blue circles in Fig. 2b and 2c), the differential conductance (dI/dV) spectra was recorded by a lock-in amplifier with a modulation voltage of 5 mV superimposed on the bias voltage. The sample bias is then swept from -1.5 V to + 1.5 V in 100 steps and the current is recorded after turning off the feedback loop at ~15 secs intervals to allow the probe position on the molecule to be checked and for stable acquisition of the spectral data A dI/dV spectral curve (averaged over the four molecules shown in panel 2b and 2c) associated with resonant tunneling through a neutral C_{60} molecule is shown in Fig. 2d, where the energetic peak positions associated with highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) are clearly resolved, which is in direct contrast to the dI/dV curve acquired over the region with just disordered solvent molecules (*i.e.*, not on C_{60}; grey circles in panel 2b and 2c) as shown in Fig. 2e (grey curve). The HOMO and LUMO derived resonance states for the C_{60} molecule are centred around -0.85 eV (marked by red arrow) and +0.75 eV (marked by blue arrow) with respect to the Fermi edge, yielding a conductance gap (ΔE) of ~1.6 eV.

Previously, we were unable to measure clearly the LUMO-derived resonance states of a C_{60} molecule which was directly adsorbed on Au(111) due to substrate induced hybridisation of molecular energy levels[24] (right hand inset schematic in Fig. 2d). The present spectroscopy data and real-space images of C_{60} molecules pinned at pore fringes points to the guest molecule being located primarily on top of the host molecular matrix, similar to previous efforts where vibrionic excitations from single molecules where observed upon decoupling the molecule from metal surfaces[25]. Interestingly, when measuring the dI/dV

curves on single C_{60} molecules located several hundred nanometres away from a pore fringe such as on a flat terrace region, we were unable to measure clear signals of molecular resonance peaks and observed weak and broadened LUMO peaks. These resemble dI/dV spectra recorded over C_{60} molecules which adsorbed directly on Au(111)[24] and hence became electronically coupled to Au(111) (see Supplementary Figure 1, orange spectra) and exhibit weak and broadened spectral molecular features. This suggests that the solvent molecules tend to crowd around the pores and are sparsely distributed in other regions of the metal surface for a fixed C_{60} molecular solution concentration. Consequently, on nanoporous gold, C_{60} molecules pinned at nanopore fringes are better electronically decoupled than C_{60} molecules adsorbed on Au(111) terraces as seen from the measured spectroscopic data. We argue that the *n*-tetradecane solvent molecules preferentially adsorb at the pores, based on evidence from the spatially mapped C_{60} molecules adsorbed on a disordered array of solvent molecules at a nanopore fringe and the energetically well resolved C_{60} spectroscopic curves. Thus the network of surface-adsorbed alkane molecules provides relatively stable host sites for crowding of the guest C_{60} molecules at and around the pore fringes.

These findings then raise the important question of whether molecular crowding can be controlled and predicted based on pore geometry and host molecule-surface interactions. We first explore the relationship between pore geometry and molecular crowding dynamics by examining the real-space STM maps for any correlation between populations of pinned C_{60} molecules and pore shapes. Figure 3a is a large area three-dimensionally represented STM image with a nanopore in the centre and C_{60} molecules crowded around the fringe. The width (W) can be measured exactly but the actual depth may be greater than the measured depth (D) due to limitations in probe geometry and tunneling conditions. The size of the molecular cluster (ensemble of C_{60} molecules, were the individual components are not fully

resolved and usually comprises of ~10 or more C_{60} molecules) observed in Fig. 3a was relatively large when compared to the previous STM images (Fig. 2a) acquired over pores with smaller dimensions. A schematic is shown in Fig. 3b summarising our understanding of the observed C_{60} molecular crowding effect around nanopores with a first ordered layer and a second ad-layer of disordered solvent molecules based on the STM and STS experiments.

The large-area *in-situ* STM image, Fig. 3c shows a wide array of pores with varying width and depth. The individual C_{60} units are well resolved and reveal the local clustering of the molecules and the underlying solvent molecules. Analysis of several other STM images with similar spatial magnification are shown in Fig 2b and Fig 2c, and we were able to manually count the number of C_{60} molecules at differently shaped pores. Based on this analysis we plot the correlation between measured molecular cluster size and pore dimension (Fig. 3d). We observed a tendency for the molecular cluster size to increase as pore fringe width increases, but cluster size does not show any direct dependence on measured pore depth. To address the role of host molecule-surface interactions, we synthesised C_{60} molecular solutions with fixed concentrations (10^{-2} M) in toluene using identical synthesis methodologies. The STM data recorded on Au(111) after drop casting these solutions in separate experiments did not reveal any preferential pinning of C_{60} molecules around pore fringes and the spectroscopic data on individual C_{60} molecules showed weak spectral features reminiscent of strong metal-C_{60} coupling suggesting the absence of solvent-mediated C_{60} adsorption on Au(111) in these control experiments (see Supplementary Information Figure 1, blue spectra). This experimental finding is of fundamental significance as it strongly indicates a crucial role for the *n*-tetradecane solvent in promoting molecular crowding around confined pore fringes and maximising electronic decoupling of the guest C_{60} molecules from the gold surface. In the case of C_{60} adsorption on Au(111) when deposited from toluene

solvent we observed in a few cases that the molecules also adsorbed along the step edges on Au(111) (see Supplementary Information, Figure 3).

To further understand and quantify molecular crowding as a function of pore fringe width we rely on atom-scale molecular dynamics simulations, which reveal ordering of the alkane solvent molecules at pores and quantify the associated damping of C_{60} molecular motion. We immerse 165 C_{60} molecules in bulk $C_{14}H_{30}$ and place the solution on top of a large-area (8 nm x 8 nm) gold substrate that contains both terrace and porous regions (Fig. 4a-f). We modelled the assembly of the solution on the substrate using 50-nanosecond simulations for each of the three 800 nm^3 cells (P1, P3 and P7, to model three of the pores measured in Fig. 3d). Full details of the models, simulation protocol, complete dataset including control simulations, and extended discussion are provided in Supporting Information. In brief, the simulations data summarised in Table 1 indicates that (1) the molecular motion of solvent molecules in the pores remains well below that of bulk $C_{14}H_{30}$ liquid, indicating the assembly of an ordered network of solvent molecules in the pores, and (2) the C_{60} molecules show a tendency to form rings on the nanopore fringes. These pore-bound C_{60} molecules have calculated adsorption energies similar to those of the C_{60} molecules adsorbed on gold terraces but, crucially, the motion of the near-pore C_{60} molecules is significantly reduced relative to motion on terrace sites, with C_{60} centre of mass fluctuations approximately halved, from 1.3 Å to 0.6 Å. Future studies could extend to microscopic timescales [26] to allow calculation of self-diffusion coefficients of solvent and solute molecules in the vicinity of the pores. Taken together, the computed molecule-pore binding energies and molecular dynamics indicate that solvent ordering at pores introduces a novel feature for C_{60} crowding whereby the molecules are slowed by decreasing the degrees of freedom of their surface motion.

Through the combined efforts of liquid-based scanning probe microscopy experiments and molecular dynamics simulations at nanosecond time scales, we can now account for a two-layer crowding mechanism for molecular dynamics at solid-state nanopore fringes at room-temperature. The solvent film formed by *n*-tetradecane in and around the nanopores strongly influences the local adsorption profile and hence molecular electronic structures recorded at the nanopore fringe sites. In particular, the population of C_{60} molecules scales almost linearly with the geometrical width of the pores as the curvature of the gold is reduced thereby strengthening the solvent-gold adhesion. In general, our findings suggest that in addition to probing energetically stable molecular end configurations more efforts from an experimental perspective are required to better understand the effect of surface defects and environmental constraints on kinetically trapped metastable molecular structures. Such insights at the molecular scale will be meaningful impact in the rational design of high performance tunnel junction devices[27], diodes[28], rectifiers[29] and transistors based on molecular ensembles[30].

Competing Financial Interests

The authors declare no competing financial interests.

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Figure Captions

Figure 1: Sketch of crowded molecular systems probed using liquid-based STM/STS. (a) Schematic of closely packed C_{60} molecules with excluded volume and overlapping volume. The hard sphere diameter (HS_d) is the measure of atomic nucleus to atomic nucleus distance and the van der Waals diameter (VDW_d) includes the enveloping electron clouds.

The delicate balance between excluded volume and hardcore interactions determines if a molecular system is sparse **(b)** or densely packed **(c)**. **(d)** Schematic of the liquid-based STM system where electrons tunnel from the metal tip-apex into the conductive sample through a liquid medium to establish stable imaging and spectroscopy conditions. **(e)** Energy diagram of the electronic states in a non-polar liquid STM junction, where the application of a voltage between the tip and the sample triggers electrons to tunnel through the liquid barrier where the tunnel current is proportional to the integral of the density of states of the conductive sample.

Figure 2: Energetics and dynamics of single-molecules at nanopore fringes. (a) Large area constant-current STM image of C_{60} molecules adsorbed on Au(111) showing a crowded configuration that lacks orientational order. (Scale bar: 5 nm, tunneling parameters: V_{bias}: 250 mV, I_t: 65 pA). **(b)** and **(c)** Constant-current STM image recorded over a sparsely populated area of panel a showing a nanopore surrounded by three C_{60} molecules and a single C_{60} molecule, respectively. (Scale bar: 1 nm, tunneling parameters: V_{bias}: 100 mV, I_t: 4.5 pA for both panel b and c). **(c)** Spatially averaged differential conductance point spectra (dI/dV signal) measured over the C_{60} molecules. (Feedback loop parameters I= 100 pA, V= 1 V). The molecular resonance peaks are resolved spectroscopically and the electronic resonances are identified as HOMO (red arrow), LUMO (blue arrow) and LUMO+1 (green arrow). **(d)** dI/dV spectra acquired on blank Au(111) (pink spectra) and on the *n*-tetradecane solvent molecule adsorbed on Au(111) (grey spectra, acquired on a region marked with grey spheres in panel **b** and **c**. (Feedback loop parameters I= 100 pA, V= 1.2 V). The left and right hand inset panels show respectively clean (solvent screened) and substrate broadened molecular energy levels.

Figure 3: Pore dimension modulated molecular crowding. (a) Wide-angle STM image of a nanopore (width: 6 nm) with molecules crowded around the fringes (tunneling parameters V_{bias}: 150 mV, I_t: 25 pA) and corresponding sketch of the observed real-space molecular and nanopore structures **(b)**. **(c)** Constant-current STM image showing variance in molecular population at pore sites with varying circumference and depths (Scale bar: 1 nm, tunneling parameters V_{bias}: 150 mV, I_t: 25 pA). **(d)** Statistical analysis of C_{60} molecular cluster size as a function of pores with varying geometry. The actual width (W) and depth (D) of the numbered pores are as follows. Pore 1 (P1): W: 2nm, D: 1nm, P2: W: 3nm, D: 1nm, P3: W: 4nm, D: 1nm, P4: W: 5 nm, D: 2 nm, P5: W: 5 nm, D: 3 nm, P6: W: 7 nm, D: 3 nm, P7: W: 7

nm, D: 3 nm, P8: W: 9 nm, D: 4 nm, P9: W: 10 nm, D: 3 nm, P10: W: 12 nm, D: 4 nm). The size of the molecular cluster increases as a function of pore width but does not show any dependence on pore depth.

Figure 4: Simulations of C_{60} dynamics at solvated nanopores. (**a-f**) Final computed structures of the interface between C_{60} molecules and porous gold, modelled in bulk *n*-tetradecane liquid using atomic-scale molecular dynamics simulations. Shown are top-down views of the pore and cross-sections through the pore, with near-gold (within 0.5 nm) C_{60} and *n*-$C_{14}H_{30}$ molecules shown in ball-and-stick representation, and gold atoms shown as space-filling spheres with an overlaid surface to emphasise the shape of the pore. Some of the more-distant *n*-$C_{14}H_{30}$ molecules are shown as transparent ball-and-sticks. The simulations replicate the experimental setup; C_{60} molecules are deposited from the liquid-phase (note the concentration of the simulation cell is 0.35 M, roughly one order of magnitude higher than in the experiments, to ensure surface adsorption within few nanoseconds computational time; 165 C_{60} molecules in 800 nm^3 of $C_{14}H_{30}$) onto the solid metal platform that contains a nanoscale pore of varying widths and depths (**P1**: width=2nm, depth=1nm; **P3**: width=4nm, depth=2nm; **P7**: width=7nm, depth=3.5nm, following the pore numbering used in Fig. 3), and the structure and dynamics of the molecules are recorded as they diffuse freely over 50-nanoseconds of room temperature dynamics. Note: we find a very small population of directly bound C_{60}-Au complexes in the MD simulations and we map using dispersion-corrected DFT the energy surface for such translocation of C_{60} into the pore *via* migration along gold (see Supporting Information).

Table 1: Calculated adsorption energies and motion (root mean square fluctuations, RMSF) of $C_{14}H_{30}$ solvent molecules and C_{60} molecules on porous gold.

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